Materials for Pumping Seawater and Media with High Chloride Content

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The problems associated with the choice of materials for pumping these liquids are explained, with particular regard to those containing hydrogen sulphide. The characteristics of the corrosion forms occurring during the pumping of such media govern the measuring techniques and instrumentation for tracking these phenomena. In particular a high-velocity test rig developed very recently is described. On the strength of their own measurements as well as data from the literature, the authors discuss the behaviour of pump materials in such media.

It is shown that the choice of material depends largely on the composition of the medium, in particular the H_2S content and the combination H_2S + air. In pure seawater or in pure chloride-containing media, the differences between the materials examined are relatively small. Austenitic-ferritic steels perform especially well in such media. In the presence of hydrogen sulphide the differences between the individual materials become great, and may reach a factor of 10^4 with high concentrations of H_2S. Special materials are needed for pumping such media.

Finally it is demonstrated that in media with high contents of hydrogen sulphide the attack is initiated by pitting, even at very high flow velocities.

Pumping media

Seawater or media with high contents of dissolved salts demand a high level of corrosion resistance in metallic engineering materials. Moreover when pumping such media, high relative velocities occur close to the material surface. Thus modern high-performance injection pumps like those used for handling oil-field injection water have a wide spectrum of flow velocities, with maxima possibly exceeding 60 to 70 m/s *(Fig.1)*. High velocities may bring further detriment to the material behaviour. Traces of contaminants in the pumping medium may also encourage the corrosive action drastically.

A distinction is made between seawater, brackish water, harbour water and oil-field water.

Seawater

Seawater at a distance from the coast contains about 3,5% dissolved salts, of which some 70 to 80% is sodium chloride. At temperatures from 10 to 15°C the oxygen content varies between 10 and 8 mg/l, the *p*H between 7,5 and 8,2. Near to the coast the aggressivity may be higher than in the open sea.

Brackish water

Brackish water is seawater mixed with river water outside harbour installations.

Harbour water

1Harbour water is heavily contaminated (by oil, wastes, sewage) river, brackish or sea water in the proximity of port installations and shipyards. Due to stagnation and inadequate aeration it may have a lower oxygen content and therefore be more corrosive.

Oil-field water

Oil-field water often has a much higher salt content than seawater: around 30% is not rare, i.e. just below the solubility limit. Here again the biggest proportion is sodium chloride. The *p*H is normally relatively low (up to about 4), so that the water reacts weakly acid. Its hydrogen sulphide content may amount to a few hundred milligrams per litre, whereas oxygen is very low or even absent.

With these media, variations in the salt content do not generallly result in a substantial change in the aggressivity. Much more important to the corrosion process are certain gases or pollutants present in the salt water, the principal ones being oxygen and hydrogen sulphide. Since these compounds will be referred to repeatedly in the following, a few general remarks on their action may be apposite.

The presence of *dissolved oxygen* is a necessary condition for metal corrosion in neutral seawater. Oxygen contents of 1 mg/l or less will still permit progressive corrosion.

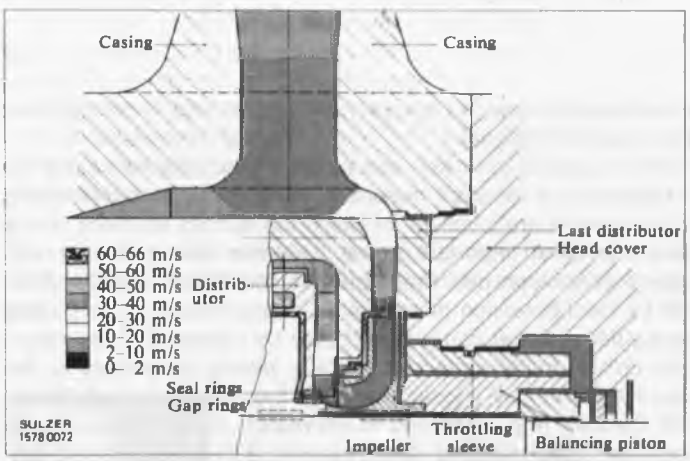

Fig. 1 Distribution of flow velocity in an injection pump.

In certain cases seawater is deaerated chemically of physically, lowering its aggressivity substantially. Maximum oxygen contents of 20 ppb (i.e. 20 mg/t) are aimed at here however. With chemical deaeration especially it must be borne in mind that the degassing takes time, and it is therefore necessary to ensure in every case that the removal or fixation of the oxygen is fully completed at the pump inlet. Here a warning must be given against possible ingress of air during operation. Even though such ingresses are usually of short duration, they may cause serious material damage in a very short time. Since the intrusion of air during operation cannot be ruled out completely, the material must be selected as though water containing oxygen were to be handled.

Seawater normally contains no *hydrogen sulphide*. On the other hand, harbour water and especially oil-field water may often contain considerable amounts of dissolved hydrogen sulphide. It is mostly organic in origin and traceable to anaerobic biological

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decomposition processes. These waters have a slightly acid *p*H (up to about 4.0) and are largely free of oxygen. Hydrogen sulphide or the sulphide ion are capable of depolarizing both the cathodic and the anodic partial reactions of the corrosion process. Tests have shown [1] that already very small quantities (less than 1 mg H_2S/l) of dissolved sulphides are capable of effecting detrimentally the corrosion behaviour of metals of the iron group (iron, cobalt, nickel) and their alloys. Above all in the presence of sulphides the passivation of these metals is rendered difficult or impossible, while the danger of local corrosion (pitting, crevice corrosion) increases.

Acid salt solutions containing hydrogen sulphide are highly corrosive and call for the use of special materials.

As further dissolved contaminants, brackish and harbour waters may contain small amounts of *ammonia* or ammonia compounds. Ammonia can cause stress-corrosion cracking in brass in a very short time. This phenomenon, known as 'season cracking' to shipping, affects seawater coolers with brass tubes especially, though not hydraulic machines because these do not usually employ brass as material.

Corrosion forms

The following forms of corrosion may occur when pumping seawater or media with high salt contents:

- Uniform general corrosion
- Pitting
- Galvanic corrosion
- Crevice corrosion
- Erosion corrosion
- Cavitation corrosion
- Stress-corrosion cracking or vibration crack corrosion

While the first three corrosion forms can be countered to a large extent by the choice of material alone, in the other destruction processes the design often plays a part no less important than the choice of material.

Uniform general corrosion can be prevented relatively easily by adopting more resistant materials. In many cases passivatable alloy systems are involved, of which the various stainless steels form the most important group. However owing to incorrect choice or inexpert use, these passivatable alloys may be affected by local corrosion mechanisms, characterized by very rapid propagation. *Local corrosion* [2] may be caused by local changes on the metal surface itself (e.g. *pitting* on defects in the passive film) or by a local change in the chemical properties of the medium (e.g. *corrosion in crevices).* At the anode of the local element formed, a low *p*H (2.5 to 3.0) is established gradually. This is confined to a small surface zone, in which the metal is actively corroded.

The danger of local corrosion is encountered particularly in still seawater. Standby pumps operated only intermittently are especially at risk. Flooding with freshwater after decommissioning or regular periodic commissioning is necessary therefore.

Galvanic corrosion is the form where two metals or electron-conducting solids of different electrochemical potential are located in the same electrolyte and connected with each other electrically. It is unimportant whether this electrically conductive connection is inside or outside the electrolyte. A corrosion element is formed, with the anode attacked more and the cathode less severely than in the unconnected state.

Owing to the high electrical conductivity of seawater and salt solutions, pumps may be produced only from similar materials. If dissimilar materials have to be used for design reasons, the wetted surfaces of the less noble metal must be large in relation to the surface of the nobler metal. When considering the so-called electrochemical series, it should be noted that the stated potentials indicate the direction of the current in the galvanic element but not the absolute rate. Furthermore high flow velocities may lead to substantial potential shifts.

Modern hydraulic machines for handling seawater and similar feature high relative velocities between the metal surface and the medium. Accordingly there is a strong interaction between mechanical erosion and corrosion, the latter being assisted by mechanical destruction of protective and covering layers. In such cases, hydraulic machinery can be operated safely only if the materials employed possess adequate resistance to *erosion corrosion.*

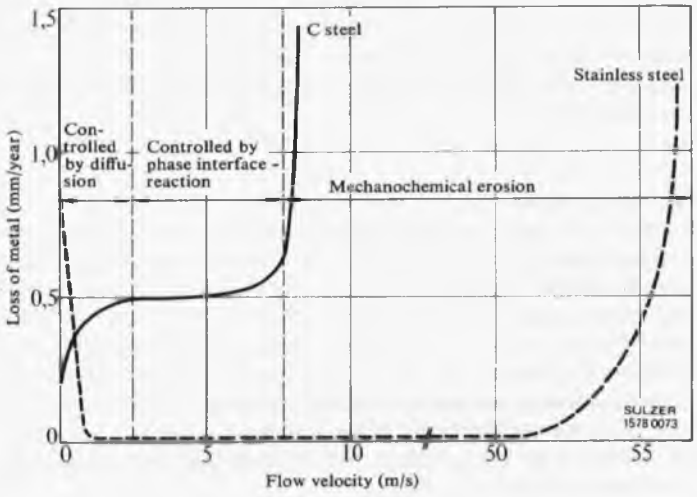


Fig. 2 Flow velocity versus metal corrosion.

Figure 2 shows the influence of the flow velocity on the removal of metal. Three zones can be distinguished with non-passivatable alloys (solid curve). In the area of low flow velocities the erosion increases with rising velocity, the corrosion being determined by the supply of oxygen (diffusion-controlled partial step). After this comes an area in which a further rise in the flow velocity does not bring any increase in the material removal rate, the corrosion being controlled by the speed of the chemical reaction at the phase interface. Above a critical threshold an increase in the flow velocity causes a steep rise in the removal rate: erosion corrosion commences, marked by a pronounced localization of the attack.

The behaviour of passivatable materials is characterized by the broken line in *Figure 2.* Here two peculiarities are conspicuous:

- At very low flow velocities the loss of material is very high (localized corrosion in almost stagnant media).
- With rising flow velocity the loss of material diminishes first (passivating action of the oxygen supplied), then after exceeding a threshold velocity it rises again steeply owing to erosion corrosion.

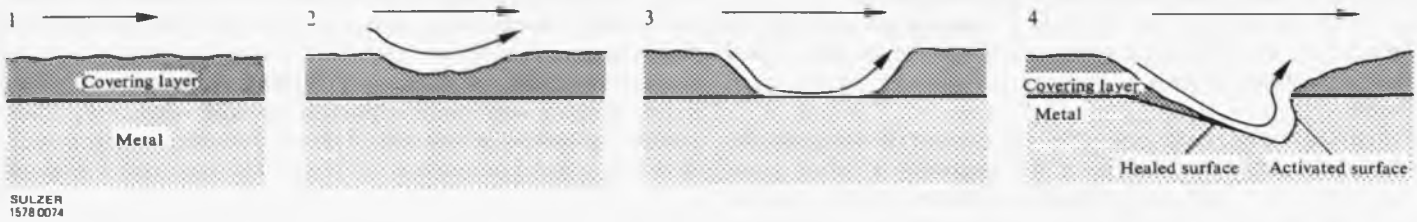


Fig. 3. Progress of erosion corrosion.

Figure 3 shows the mechanism of erosion corrosion attack. In a still or slowly flowing liquid a metal is normally protected by a covering layer. If the flow velocity is raised, the covering layer starts to break away until the bright metal is exposed, whereupon this starts to corrode. A hollow is worn away, altering the flow profile. At the less prominent places a healing process takes place, and the passive layer is able to form again, but the exposed places are attacked more severely. In this mechanism the mechanical element predominates. It will be obvious, however, that increasing the flow velocity will also accelerate the chemical corrosion component, because the movement of the co-reactants to the surface and the reaction products from the surface is accelerated.

The bubble implosion associated with *cavitation corrosion* and the attendant destruction of metal are not peculiar to the media under discussion here. However owing to the aggressiveness of these media the consequences of liquid cavitation may be serious. Due to the implosion of bubbles in the immediate proximity of the metal surface, the protective covering layer is destroyed and the mass transportation processes are accelerated by the reduction of the boundary layer thickness, so that the metal surface is accessible to uninhibited active corrosion as well as the mechanical destruction.

Cases of *stress-corrosion cracking or vibration crack corrosion on stainless steels are* almost unknown on pumps handling seawater and solutions with high salt content. Two reasons can be given for this:

- The temperature of the medium is usually below 65°C (stresscorrosion cracking normally appears only at higher temperatures) [3].
- The materials used are in the form of castings for the impeller and casing, which have a much higher resistance to stress-corrosion cracking than rolled material of similar composition for example [4].

Pump shafts may sometimes sustain a vibrating stress, which must be allowed for in the design, by avoiding sharp-edged transitions for instance. Moreover it must be ensured that the materials employed have adequate resistance to pitting, because pitted areas may produce a notch effect that is not to be underestimated, especially on steels of high tensile strength.

Procedure for choice of material

Apart from establishing the chemical properties of the materials considered with regard to corrosion, their behaviour in relation to erosion corrosion is of prime importance.

Various rigs are employed in the laboratory for investigating the behaviour of materials in fast-flowing media, for example the rotating disk, rotating cylinder, coaxially arranged cylinder or flow-swept tube.

Figure 4 shows a measuring facility for recording electrochemical current density/potential curves by means of rotated disk. With this apparatus – a rebuilt precision boring machine with shaft drilled through and mercury contact – velocities of about 15-18 m/s can be reached. As a rule, however, the facilities mentioned will rarely allow flow velocities beyond 20-30 m/s because vibration and turbulence cause considerable disturbance and falsify the processes; they may even lead to cavitation phenomena. These disadvantages could be largely circumvented with the construction of a novel testing machine – a SULZER development – which has already been described more than once in the literature [5, 6].

The test rig *(Fig.5)* may be regarded as a pump with diskshaped impeller. The maximum speed of this impeller, driven by a 20 kW direct current motor, is 8000 rev/min, equivalent to a peripheral speed of about 100 m/s. As the rig operates in a closed circuit, measurements can be made also with controlled gas content (e.g. with adjusted oxygen or hydrogen sulphide content). Hydraulically the system may be considered as a straight-line Couette flow with a Reynolds number given bij the following equation:

$$Re = \frac{u \cdot R}{\nu - 1}$$

u Peripheral speed (cm/s)
R Impeller radius (cm)
ν Kinematic velocity (cm²/s).

The exponent characterizing the correlation between mass transport and speed has been established experimentally as 0.38 [6].

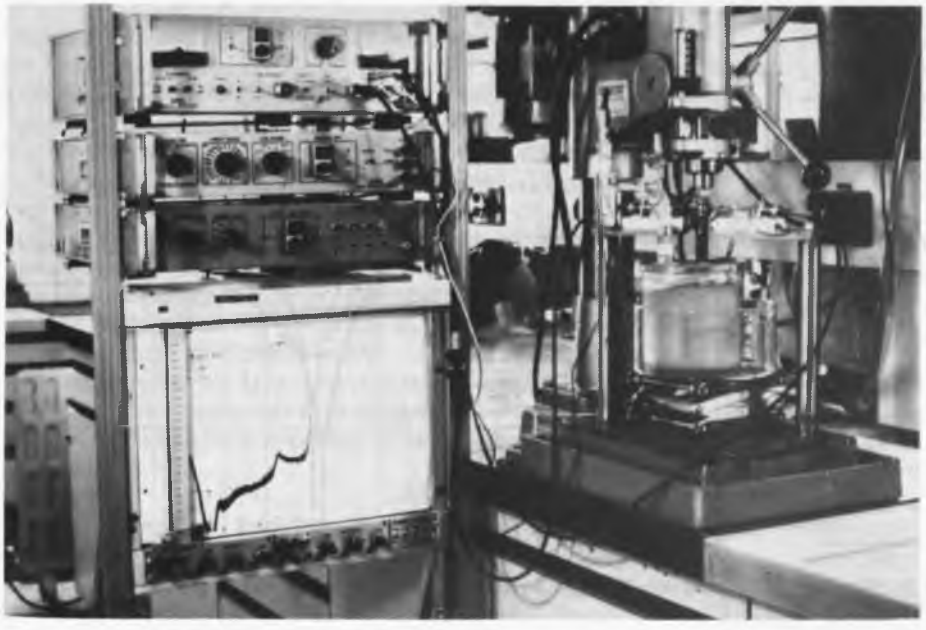


Fig. 4. Setup for electrochemical measurements at high flow velocities with a rotated disk (left: electrochemical apparatus for recording potential/current density curves; right: precision boring machine with rotated disk and measuring cell).

Fig. 5. High-velocity testing machine (left: dc motor; right: casing with disk-shaped impeller).

Table 1: Loss of material in media with high chloride content (measuring duration: 200 h at least, μ = 40 m/s, T = 50 °C)

pH	Gas introduced	H_2S content (ppm)	Loss of material ($g/m^2 \cdot d$) X6 CrNiMo 18 12	X5 CrNiMoNbN 229	X8 CrNiMoCu 25 5	X3 CrNiMo 26 5	G-X5 CrNiMoCu 21 8	CrNiMoCu 21 8	G-X5 CrNi 13 4	G-X5 CrNiMo 17 4	X6 CrNiMoCu 14 5
7.8	O_2		4.0						17.1		7.1
7.8	N_2		0.6				0.7		4.1		
5.5	N_2						1.0				
5.5	O_2	3–16			241		34				
5.5	N_2	3–16			8.3	410	16	14			
5.5	N_2	25–53	6.3	12.5			28	23	7980	572	166
5.5	N_2	100–180	21		498		452	843			

Influence of the composition of the medium on the corrosion behaviour of pump materials

The groups of pumping media examined here differ principally in the following parameters:

- Chloride content (up to 180 g/l)
- *PH* (8.3-4)
- Oxygen content (10-0 mg/l)
- Contaminants e.g. hydrogen sulphide (0-500 ppm)

The respective influences of these parameters on the corrosion behaviour of the various materials are revealed by the following test results:

- *Table 1* shows the loss of weight by various materials at 40 m/s flow velocity as a function of the medium *p*H (here an oil-field water containing 133 g/l Cl), of the oxygen content (saturation and 25 ppb O_2 obtained by nitrogen flushing) and of the hydrogen sulphide content.
- The influence of the temperature *p*H, oxygen and hydrogen sulphide contents on the pitting propensity of an austenitic ferritic steel is shown in *Figure 6*.
- *Figure 7* plots the potentiokinetic current density/potential curves for an austenitic steel in solutions with various chloride contents. These curves were recorded at 6.9 m/s with the apparatus shown in *Figure 4*.
- *Figure 8* graphs the electrochemical behaviour of an austenitic steel as a function of the nature of the dissolved gas and its *p*H.

Table 2: Influence of the medium characteristics on the corrosion speed under steady conditions (Material: NiCu30AlFe)

Characteristics of the medium Cl content (g/l)	*p*H	Oxygen content	Relative corrosion speed
18	7.4	Saturation	1*
18	5.5	Saturation	1.3
133	7.4	Saturation	3.0
133	5.5	Saturation	3.3
133	5.5	Nil	0.1

* Corrosion speed in pure seawater

Whereas the test results listed above refer almost exclusively to passivatable chromium-nickel steels, *Table 2* shows the influence of the same medium parameters on a Ni-Cu-based alloy.

The following facts emerge from these results:

- Increasing the chloride concentration above 18 g/l leads to a steep rise in the corrosion speed.
- Bij lowering the oxygen concentration from saturation to about 25 ppb the corrosion behaviour of passivatable stainless steels is affected only little: the electrochemical measurements indicate only a very indistinct narrowing of the passive range and a rise in the activating current. In this range the influence of the oxygen concentration on local corrosion is likewise negligible. On the other hand, with alloys containing copper the oxygen content plays a more important part. Quite generally its influence increases as the corrosion resistance

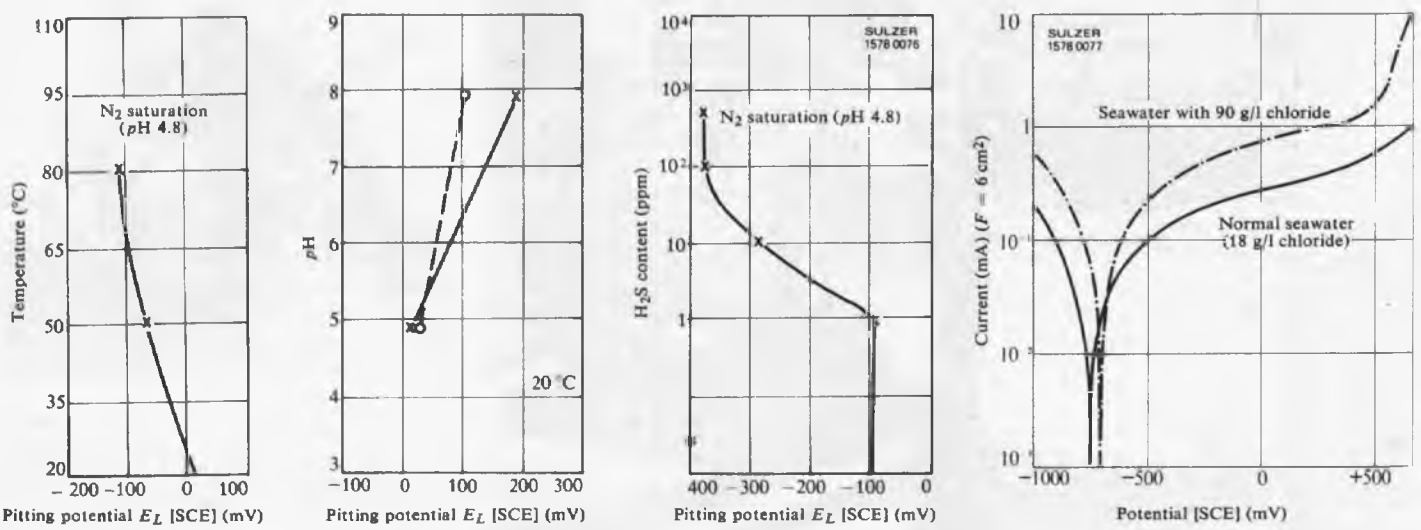
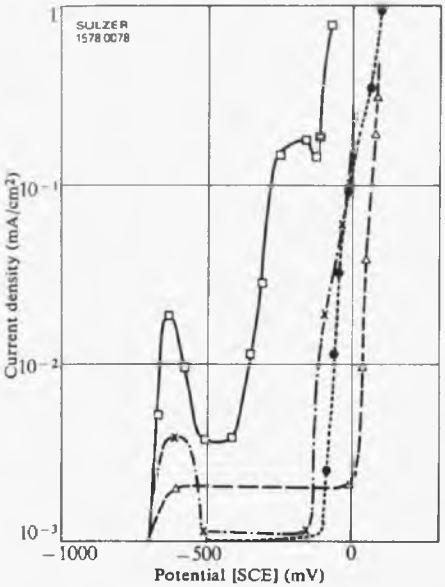


Fig. 6. Influence of temperature, nature of gas introduced and H_2S content on the pitting potential E_L of the austenitic-ferritic steel G-X6CrNiMoCu218.

Fig. 7. Influence of the chloride content on the behaviour of steel G-X6CrNiMo18 10 in flowing electrolyte (V = 7 m/s, room temperature).



●····● O_2 saturation, *p*H 7
△ – – △ N_2 saturation, *p*H 7
×–·–× N_2 saturation, *p*H 5
□——□ N_2 saturation, *p*H 5
1000 ppm H_2S

Fig. 8. Anodic partial curves of austenitic steel X5Cr NiMoNb22 9 in media with high chloride content (T = 50°C).

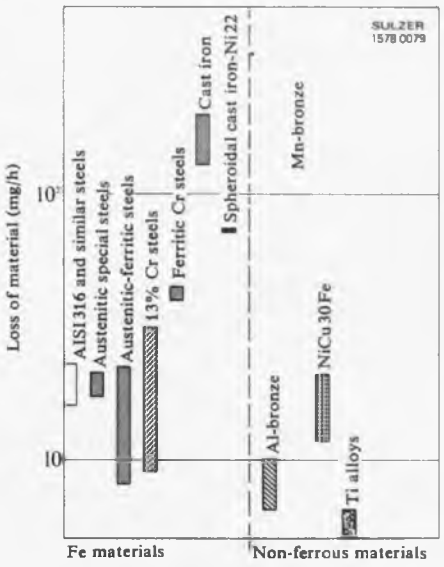
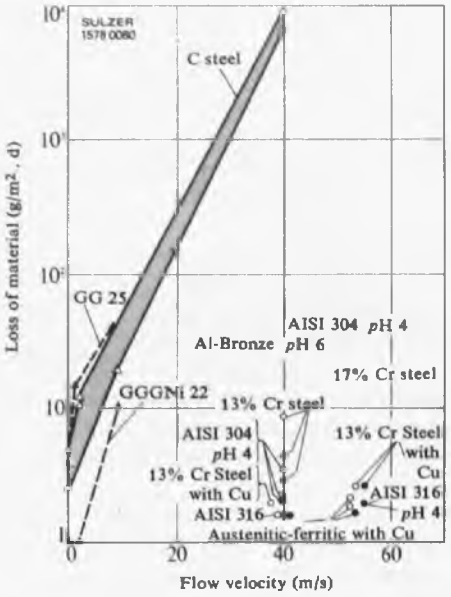


Fig. 9. Loss of pump materials due to cavitation in seawater.



○ Oxygen saturation
○ Oxygen content < 25 ppb
○ Oxygen content < 5 ppb
(if not otherwise stated, *p*H about 7.8)
○◑● Own measurements
▲ According to INCO [3]
△ According to Stahl und Eisen [21]

Fig. 10. Loss of pump materials in seawater.

of the material becomes less.
- In the range of 5.5-7.8 the *p*H influences the corrosion resistance of the materials examined only little, though this is true only of media with low hydrogen sulphide content however.
- The loss of material under high flow velocities is influenced decisively by the presence of sulphides. This is due to the fact that the H_2S and HS- compounds are adsorbed correspondingly, while the H_2O molecules or OH- ions respectively are displaced to the surface. As a result, sulphide layers are formed with properties favouring corrosion (good electrical conductivity, defective crystal structure, small overvoltage for hydrogen developement with resultant increase of the diffusion limit current).

However H_2S and HS_1 compounds are stable only with a limited *p*H range: above a *p*H of 12 to 13 only S =ions are present [7]. Consequently in strongly alkaline salt solutions no detriment to the corrosion resistance is to be expected. With falling *p*H, on the other hand, HS- ions and H_2S become thermodynamically stable, so that the corrosion speed increases. The amount of this rise depends on an interaction between the formation of sulphide covering layers and their adhesion [8]; with *p*H 7 the adhesion of the covering layers is generally good and these are formed at a constant rate, so that corrosion will be very low. Further lowering of the *p*H leads to impaired adhesion and hence to accelerated corrosion [9].
The properties of the layers formed are influenced by the ionic strength of the medium among other things. According to [10] the formation of stable sulphides in salt water ought to be impossible.

From what has been said, therefore, and from the experimental results, it is clear that with regard to the choice of material a distinction must be made between the following groups of media:
1. Seawater or chloride-containing media with varying chloride content (*p*H between 5.5 and 7.8 or higher) free of other contaminants. This group includes all seawater except from harbour areas, which may be heavily contaminated.

Material No. to DIN 1707	Material designation to DIN 17006	Further designations, remarks
Austenitic nickel cast iron		
0.6655	GGL NiCuCr15 6 2	NiResist 1
0.6660	GGL NiCr20 2	NiResist 2
0.7660	GGG NiCr20 2	NiResist D2
Martensitic and ferritic stainless steels		
1.4021	X20Cr13	
1.4034	X40Cr13	
1.4313	G-X CrNi13 4	A296 Grade CA-6 NM
1.4057	X22CrNi17	
1.4059	G-N22CrNi17	
Austenitic stainless and special high-alloy steels		
1.4404	X2CrNiMo18 10	Type AISI 316
	G-X3CrNiMo20 10	A269 Grade CF-3 M
1.4408	G-X6CrNiMo18 10	Type AISI 316
	G-X8CrNiMo20 10	A296 Grade CF-8 M
1.4500	G-X7NiCrMoCuNb25 20	
1.4539	G-X2NiCrMoCu25 20	
1.4550	X10CrNiNb18 9	
1.4552	G-X7CrNiNb18 9	
1.4571	X10CrNiMoTi18 10	
1.4577	X5CrNiMoTi25 25	
	X6NiCrMoCu35 20	CN7M (Alloy 20) IN-862 V-90 V-93
1.3974	X3CrNiMoNbN23 17	
Austenitic-ferritic steels		
	G-X5CrNiMoCu21 8	Ferrite 52–58%
	G-X8CrNiMoCu25 5	Ferrite 65–70%
1.4460	X8CrNiMo27 5	Ferrite 40%
Copper alloys		
		Monel Alloy 400 Monel Alloy K 500
2.0975 01	G-CuAl10Ni	Inoxyda 90
2.0975 04	G-CuAl10Ni G-CuAl9Ni	Inoxyda 53 H

Table 3: Typical materials for pumping systems handling seawater and media with high chloride content

2. Seawater or chloride-containing media as under 1. (*p*H between 5 and 7) and hydrogen sulphide content up to about 150 ppm, free of O_2.
3. Seawater or chloride-containing media as under 2., but containing O_2.
4. Seawater or chloride-containing media (*p*H between 4 and 5.5) with hydrogen sulphide up to 500 ppm.

It should be noted that media of group 3 hardly occur in nature. They result only when pumping media of group 2 due to ingress of air into the pumping system. The remarks that follow will deal with the behaviour of pump materials in these media.

Materials for pumping seawater

Although economic aspects (material procurement costs, machining costs) are not emphasized in this article, it is not proposed to enlarge upon exotic materials. Accordingly the remarks that follow will deal primarily with conventional pump materials. *Table 3* gives a survey of the materials used or usable in pump engineering. The behaviours of the individual materials in the media described are then discussed, dealing in particular with the resistance to the principal forms of corrosion.

Behaviour of materials with regard to local corrosion

Table 4 sets out data on the behaviour of materials with regard to local corrosion. It will be seen that in each of the three structure classes (austenitic, ferritic, ferritic-austenitic) materials are to be found assuring excellent resistance to local corrosion. Steels with partially or fully austenitic structure give good resistance to local corrosion only if the sum of Cr% + 3.3 Mo% is at least 30%. Unsatisfactory resistance is revealed by the ferritic steels: only by adding nickel is their behaviour improved clearly [12, 13].

Informative are the results of [14], demonstrating that the resistance of Mo-free steels in Cl-containing media is poor. Mo improves the behaviour of the steels, but the usual additions of 2,5 to 2,8% are not enough. Only with Mo contents above 5% is the resistance of the steel improved significantly. Cu coatings, even though porous, decisively improve the resistance of the steels to local corrosion. This observation is very interesting, because it partly explains the fact that additions of Cu improve the resistance of some steels.

Behaviour of materials under cavitation and cavitation corrosion

Figure 9 shows the loss of material due to cavitation. It is evident that the cavitation resistance of the materials examined covers a more or less wide scatter range, depending not only on the chemical composition but also on the different heat teratments.

Steels with austenitic-ferritic mixed structure and stainless martensitic Cr steels have good resistance, whereas ferritic chromium steels behave badly. Of the non-ferrous materials, aluminium bronzes and titanium possess high cavitation resistance.

The cavitation resistance in seawater is determined by the corrosion resistance and by the physicometallurgical properties of the materials, the influence of the latter increasing as the cavitation becomes more intensive. Even under intensive cavitation, however, the influence of the chemical properties is still strong. Thus corrosion-resistant materials like AISI316 steel or NiCu 30Fe suffer loss of material in seawater 18 to 22% higher than in a non-corrosive medium such as distilled water. With less corrosion-resistant materials like spheroidal cast iron with 22% Ni, the difference may widen to as much as 37%.

As far as the physicometallurgical properties are concerned, materials possessing good ductility *as well as* high strength with great hardness will display good cavitation resistance.

With regard to the influence of the structure, cubic face-centered lattices (bronze, austenite, etc) behave better than cubic body-centered or hexagonal ones (ferrite, etc [20]). The materials of the first group can sustain more plastic deformation before the onset of damage by cracking. On the other hand, the second group reveals no significant plastic deformation. Here the cracks are almost always at right angles to the workpiece surface, so that the fracture includes undamaged grain conglomerates too.

Table 4: Behaviour of materials with regard to local corrosion

Abbreviated designation (nearest DIN equivalent)	Typical pitting rate (µm/a)	Activated *p*H value [11]	Pitting potential at 60 °C (mV[SCE])
Austenitic materials			
X5CrNi189 (1.4301)	1780–6350 [3]	3.5	
X5CrNiMo18 12 2.5 (1.4401)	1530–2870 [3]	3	+120 [15]
			+200 [16]
Ni-Resist 1.2	50–100 [3]		
X6CrNiMoTi18 8 2.5	~500 [13]		+100 [17]
X3CrNiMoCu18 16 6	<100 [13]		
X2CrNiMoCu20 25 5 (1.4539)		1.5	
X2CrNiMo18 16 3 (1.4438)			+120 [17]
X2CrNiMoN17 13 5 (1.4439)			+180 [17]
X4CrNiMo18 12 3 (1.4436)			+120 [18]
X4CrNiMo18 12 3 (Mn<0.3)			+340 [18]
X3CrNiMoNN23 17 (1.3974)			+240 [19]
Austenitic-ferritic steels			
G-X5CrNiMoCu21 8 (ferrite 52–58%)		2	
X3CrNiMo26 5 1.5 (1.4460)			+450 [15]
Ferritic steels			
X1CrMo261	>1000	2	
X1CrMoNiNb28 2 4 (1.4575)			+500 [17]
Other ferrous materials			
Cast iron, SG iron	100–300 [3]		
Non-ferrous materials			
NiMo16Cr (Hastelloy C)	0 [3]		
NiCu30Fe	130–180 [3]		
Titanium alloys	0 [3]		
Aluminium-bronze	50–230 [3]		

Behaviour under flowing seawater

The correlation between loss of material and flow velocity is graphed in *Figure 10*, which is based on data from the literature and results of our own. Some measured values show the influence of the *p*H, and oxygen content moreover. The influence of the two latter parameters is evident from *Table 1*, which allows a comparison of the behaviour of the material in normal seawater and a contaminated acid medium. From these data the following conclusions may be drawn:

- With corrosion-resistant materials an oxygen content of less than 5 ppb is already sufficient to enable passive layers to form. With less corrosion-resistant materials like 13% Cr. steels for example, the depolarizing action of an increasing oxygen content on the cathodic partial reaction predominates. Accordingly the corrosion rate quickens with increasing oxygen content.
- The resistance of 13% Cr steels is improved by adding copper.
- With corrosion-resistant materials, *p*H changes in the range of 5-7.8 have only a minor effect. It is difficult to establish a resistance sequence for such materials, at least under flow velocities up to 55 m/s, because the loss rates of austenitic or austenitic-ferritic steels are very low. One exception is spheroidal cast iron with 20% Ni, which performs unsatisfactorily despite its austenitic structure.
- Non-alloy steels or cast iron become unusable already at low flow velocities.

For the pump designer it is less important to know the absolute loss of material at different flow velocities than the critical flow

velocity, above which erosion corrosion commences. The critical flow velocity is a value which must not be exceeded on any part of the pump.

Figure 11 illustrates the significance of the critical velocity. The specimen on the left did not reach this, and is largely intact. Raising the velocity to 70 m/s (above the critical threshold) led to rapid destruction of the specimen, however. In both cases the measuring time was 200 h. Our own measurements revealed no material damage oriented in the flow direction. Even on the materials of lower corrosion resistance the attack was unaffected by the direction of the flow, though grooves from machining are preferred points of attack.

It thus seems that the usual mechanism of erosion corrosion, derived from experience with soft materials like copper, does not hold good for stainless steels – at least in the flow range investigated.

Materials for pumping contaminated chloride-containing media

Table 1 and *Figure 12* show some test results to media with low H_2S concentrations (up to about 100 ppm). It is clear that the loss of material is governed largely by the H_2S content in the solution. It was shown that at low H_2S contents (up to about 60 ppm) the corrosion speed (V) increases linearly with the H_2S concentration Cs. A similar linear correlation was found by L. Hackl and co-workers [22]. On the other hand with higher contents:

$$V = f(C_S)^{1.3-1.7}$$

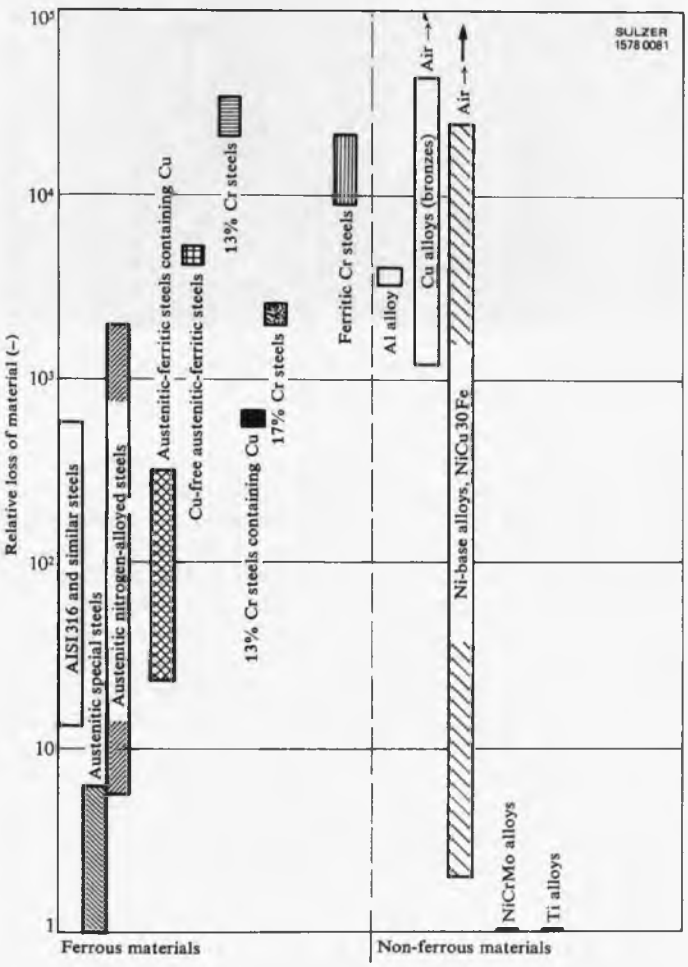


Fig. 12. Relative loss of materials in media containing H_2S (pH 5.5, T = 50°C V = 50 m/s).

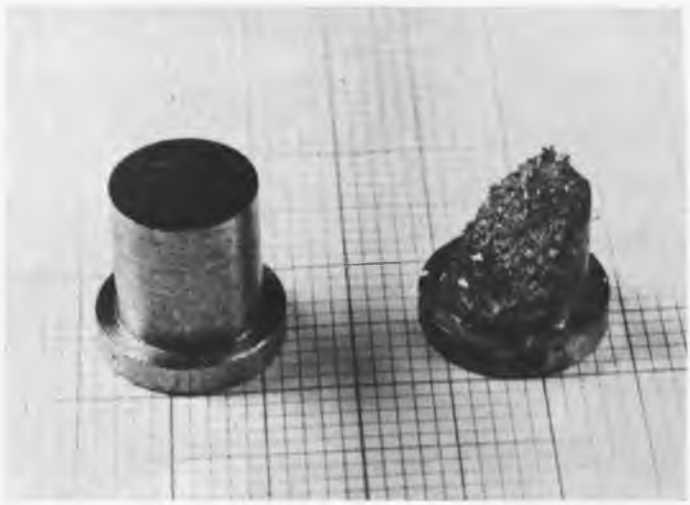


Fig. 11. Significance of the critical flow velocity for erosion corrosion on stainless steels in media containing chloride (left: critical flow velocity not exceeded; right: critical velocity exceeded). Test duration 200 h in both cases.

It is apparent moreover that the simultaneous presence of hydrogen sulphide and oxygen has a synergetic effect. Already J. F. Bates [23] established that aerated solutions containing H_2S are much more corrosive than unaerated ones.

He ascribed this to the formation of sulphidic-oxidic mixed layers with high defect number. By analogy it may be assumed in this case that oxygen encourages the formation of thermodynamically unstable sulphidic layers with incoherent structure and poor adhesion.

The sulphide influence is reflected cathodically in an increase of the diffusion limit current, and anodically in a narrowing of the passive range, a shift towards negative values and an increase in the activation current (*Fig. 8*). Less affected however is the steepness of the anodic part curves.

Moreover in many cases a first repassivation range, sometimes pronounced, is discerned at about – 500 mV, and a second one around – 200 m V GKE. The first passivation range is traced to the formation of sulphidic covering layers on the surface. The defective structure and poor adhesion of these layers are responsible for the marked narrowing of the passive range.

Here it should be noted that in contrast to oxides [10] the passivation due to the formation of sulphidic covering layers does not afford additional protection against corrosion.

The second passivation range however depends on the oxidation of the sulphidic compounds to yield elementary sulphur which is thermodynamically possible in this potential range.

The pitting potential E_l is likewise strongly influenced by the H_2S content and within the range 1-100 ppm H_2S it diminishes almost linearly with the logarithm of the H_2S concentration lg Cs (*Fig. 6*). Above 100 ppm H_2S the pitting potential does not change.

From *Figure 12* it is also evident that the differences in the corrosion behaviour of the individual materials, which are relatively small in pure seawater, may reach a factor of 10^4. As a rule austenitic steels perform well in such media though they are more susceptible to crevice corrosion. Austenitic-ferritic steels with a ferrite content up to about 60% may be used provided the H_2S content does not exceed 50 ppm. It should be noted that Cu-free austenitic-ferritic steels give a performance much inferior to those containing copper. The Cu-free austenitic-ferritic steels are damaged primarily by severe selective corrosion (*Fig. 13*).

In the literature there are already a few references to the positive influence of copper additions in steels used in media contain-

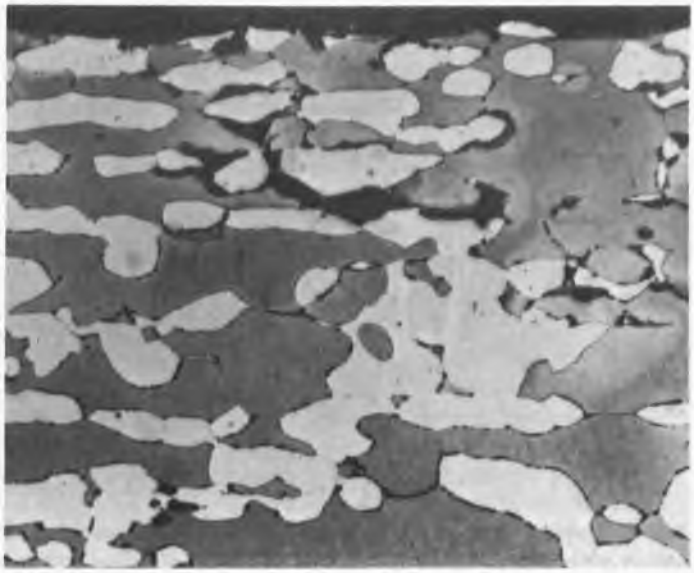


Fig. 13. Selective corrosion of the ferritic phase in a Cu-free austenitic-ferritic steel (magnification about 250x).

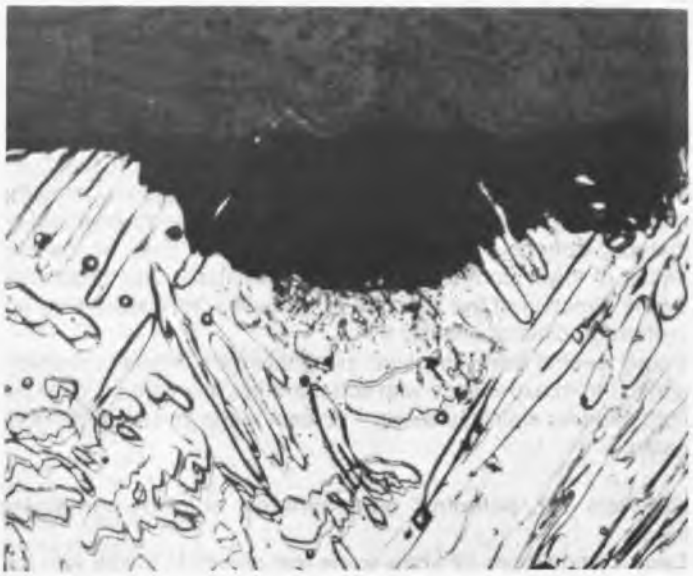


Fig. 14. Pitting on an austenitic-ferritic cast steel in fast-flowing media containing H_2S (magnification about 250x).

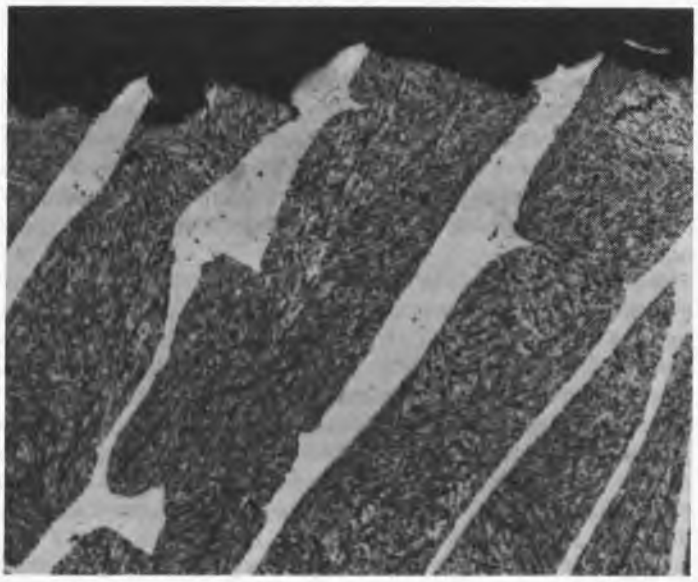


Fig. 15. Selective corrosion of the martensitic phase on a martensitic-ferritic steel in fast-flowing media containing H_2S (magnification about 250x).

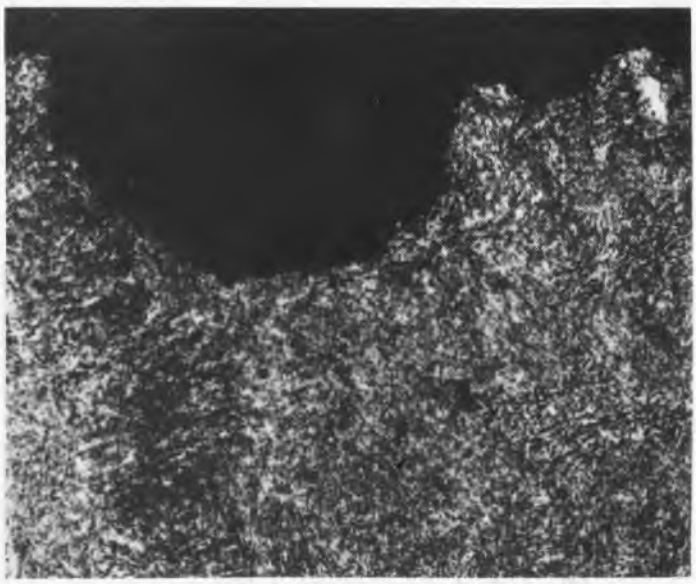


Fig. 16. Pitting on a martensitic steel in fast-flowing media containing H_2S (magnification about 250x).

ing H_2S [11, 24]. Copper heightens the action of molybdenum synergetically. In addition it reacts with the sulphidic compounds adsorbed on the surface of the specimen, forming insoluble Cu_2S and thus neutralizing the action of H_2S.

Martensitic steels cannot be used in these media as a rule. Though their behaviour may be improved substantially by increasing the Cr content and also adding copper, it does not satisfy the demands of practice.

Figures 14 to *17* show metallographic cross sections of austenitic, martensitic and austenitic-ferritic steels tested under high flow velocities in media containing H_2S.

Experience with media of this kind shows that even at high flow velocities the attack proceeds selectively similar to pitting. This is shown in *Figure 18* on a stainless martensitic Cr. steel by way of example; the original pitting gradually leads to whole areas of the surface crumbling away. This observation is at variance with previous understanding, which regarded such localized corrosion forms more as a characteristic of stagnant media.

For non-ferrous metals the same reasoning holds good in principle as for steels. From *Figure 12*, it is evident that with high-Cu alloys the effect of oxygen and hydrogen sulphide in combination is very marked. This can be ascribed to the weakening of the covering layers described. *Figure 19* shows that once the medium contains traces of O_2 the material NiCu30Fe reveals severe attack after a relatively short time (200 h at 40 m/s).

With still higher H_2S contents (up to 500 ppm) and lower *p*H (medium group 4) the significance of the flow velocity as a corrosion-influencing parameter increases further (*Fig. 20*). For such media therefore, only austenittee may be considered in principle. Here it should be noted that under these conditions the normal austenitic steels (e.g. 1.4408, 1.4571, etc) have a much lower critical flow velocity (around 25 m/s) and are therefore unsuitable for pumps. On the other hand, good results are obtained with special austenitic steels with high Ni, Cr. and Mo contents.

Conclusions

The choice of materials for pumping seawater and other media with high chloride content is a complex problem for the producer of modern high-performance pumps on account of the high flow

Fig. 17. Pitting on an austenitic steel in fast-flowing media containing H_2S (magnification about 250x)

Fig. 18. Attack mechanism on a Cr steel in fast-flowing media containing H_2S. First phase (left): formation of pits; second phase (right): spreading of the pits and crumbling of entire surface areas (magnification about 10x).

velocities encountered. Furthermore many media, especially water from subterranean deposits – such as oil-field water, are heavily contaminated with substances like hydrogen sulphide, which increase their corrosivity drastically. The demands imposed on the materials are correspondingly higher.

For modern pumps which are to handle such media, apart from exotic materials only high alloy steels and a few non-ferrous materials may be considered. Non-alloy or low-alloy steels and cast iron are ruled out. Even austenitic Ni cast irons may be used only with reservation, at low flow velocities for example. When choosing the material, allowance must be made in particular for the possible presence of hydrogen sulphide in the pumping medium.

It is conspicuous that on ferrous materials the attack proceeds locally even at high flow velocities, and is usually initiated by pitting or selective corrosion.

The resistance of the various materials may differ by a factor of 10^4, disregarding the non-alloy and low-alloy steels. Obviously in such cases wrong choice of material may have serious consequences.

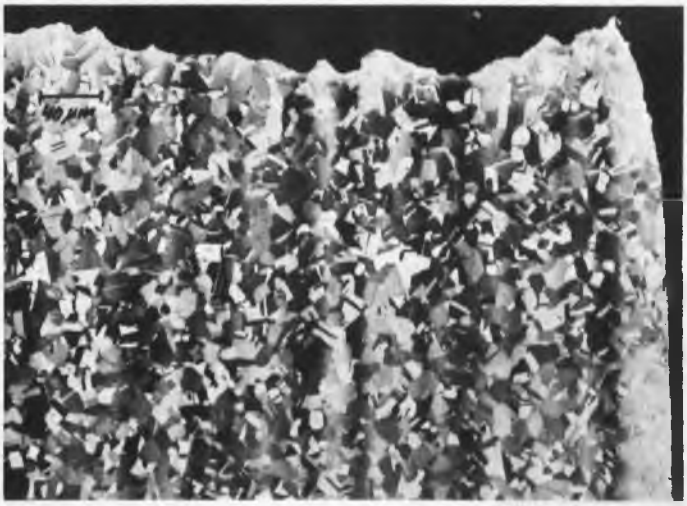


Fig. 19. Synergetic action of air and hydrogen sulphide on the loss of NiCu30Fe in fast-flowing media containing H_2S (magnification about 250x).

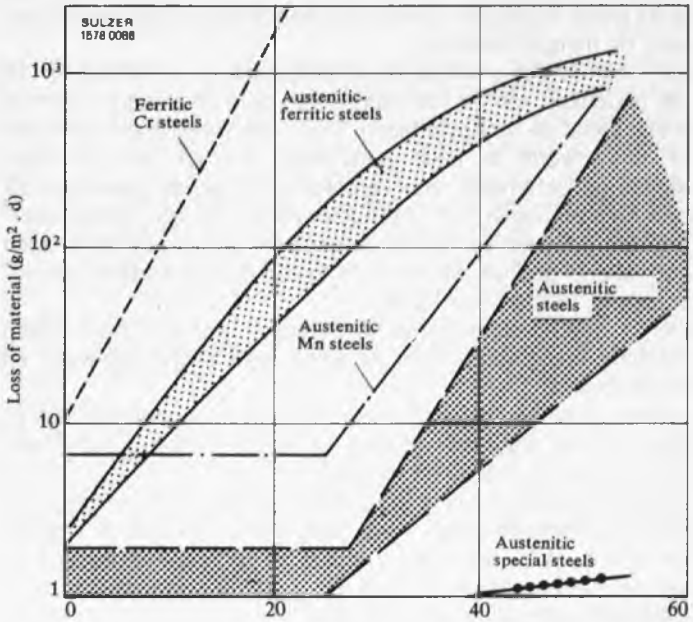


Fig. 20. Influence of flow velocity on loss of material in media with high H_2S content and low pH values.

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Boekbespreking

DE MAKENDE MENS – rond de geschiedenis van de metaalbewerker door A. J. Marx.
Jubileumboek uitgegeven door Vogel VP te Oud Beijerland, voor de firma Widenhorn bv te Rotterdam.
Afm. 19,5 × 25 × 1 cm., 128 blz. vele illustraties. Geplastificeerde paperback.
In de aankondiging is geen prijs vermeld.

Dit boek is een uitgave ter gelegenheid van het 60-jarig bestaan van de handelsonderneming Widenhorn bv te Rotterdam, een firma welke is gespecialiseerd in gereedschappen en werktuigen voor de metaalbewerking.
Het boek is vlot geschreven en behandelt de ontwikkeling van het bedenken van en het gebruik van gereedschappen door de mens vanaf de vroegste tijden. Door vele tekeningen, schetsen en foto's wordt de tekst verduidelijkt en blijkt hoe de mens steeds gezocht heeft naar verbeteringen van de gereedschappen en werktuigen voor metaalbewerking. Er zijn talrijke voorbeelden gegeven van bereikte resultaten en van de werktuigen voor allerlei gebruik die met behulp van de ontwikkelde gereedschappen werden vervaardigd.
Het is geen wetenschappelijk betoog, maar een heel prettig leesbaar boek, vooral door de vele anekdotische gegevens en de illustraties.
In een 15-tal hoofdstukken wordt de stof behandeld en niet alleen de leek, maar ook de meer ingewijde technicus zal er veel van zijn gading in kunnen vinden.
In de mij ter beschikking staande prospectus is geen prijs vermeld. Geïnteresseerden wordt aangeraden om zich te wenden tot de firma Widenhorn te Rotterdam, of tot Vogel VP Publicaties te Oud Beijerland om inlichtingen.
Een aanbevelenswaardig boekje.

prof. ir. J. H. Kr.